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TITLE:

SOLVENT EXTRACTION MIXTURE
COMPRISING SUBSTITUTED
IMIDAZOLE OR BENZIMIDAZOLE FOR
THE PURIFICATION OF GROUPS OF
BASE METALS

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SOLVENT EXTRACTION MIXTURE COMPRISING SUBSTITUTED IMIDAZOLE OR BENZIMIDAZOLE FOR THE PURIFICATION OF GROUPS OF BASE METALS

5 **[0001]** This application claims priority from PCT/ZA02/0097 published in English on December 19, 2002 as WO 02/101101, which itself claims priority from ZA 01/4793 filed 13 June 2001, the entire contents of each are incorporated herein by reference.

10 **[0002]** This invention relates to a mixture of organic compounds suitable for the solvent extraction-based separation and purification of base metals and associated impurities from weakly acidic sulphate solutions.

15 **[0003]** Hydrometallurgical methods to recover base metals from ores, concentrates or intermediates have increased in popularity due to the perceived reduced environmental impact in comparison with smelting operations. Their application is frequently hindered by the lack of suitable methods for the selective recovery of the metals of interest in a pure form.

20 **[0004]** Acidic sulphate solutions could be obtained by direct acid leaching of processing residues, ores or concentrates containing oxides and/or secondary sulphides of base metals. They could also be obtained by treating similar but more refractory materials by low pressure oxidation (Activox process), standard pressure oxidation or bioleaching of sulphides, or high temperature acid leaching of refractory oxide ores.

25 **[0005]** The resulting aqueous sulphate solution, which could also contain other anions such as chloride and nitrate, mostly contains the base metals Cu, Ni, Co, Zn, Cd and Pb, additional impurities such as Mn, Fe(II), Fe(III), and the alkaline earth metals Ca and Mg, their relative concentrations depending on the ore/intermediate being treated.

30 **[0006]** The removal of appreciable amounts of copper from such solutions can be effected by selective cementation with scrap iron or by solvent extraction (SX) with hydroxyoxime based extractants (LIX-extractants).^(1,2) In both instances, the presence of ferric ions in the leach solution will affect the efficiency of the downstream recovery process and its efficient removal is highly recommended but not always readily achieved, not even with hydroxy-oxime based extractants.

[0007] Pregnant solutions obtained by leaching zinc oxide ores or roasted sulphide concentrates or direct bioleaching of sulphides, are traditionally treated by a combination of neutralisation/precipitation and cementation to remove undesirable impurities such as Fe, Ni, Co, Cu, Cd and Pb before electrowinning (EW).⁽³⁻⁷⁾ This is normally associated with appreciable losses of zinc. More recently, SX has also been used as a means of purifying the primary leach liquor with the added advantage that the zinc content of the pregnant liquor can be increased to suit subsequent EW requirements.

[0008] The preferred extractant appears to be di-2-ethyl hexyl phosphoric acid (DEHPA) which is not very selective for zinc and tends to co-extract impurities such as Fe, Al, Pb, Cd and Ca if a raffinate with a low zinc content is required.^(8,9)

[0009] Treatment of nickel/cobalt pregnant solutions tends to be more complicated. The main impurities in such solutions are typically Fe, Mn, Ca, Mg, Cu and, to a lesser extent, Zn. The separation of nickel and cobalt can readily be effected with a SX reagent such as bis (2,4,4-triethylpentyl)-phosphinic acid (CYANEX 272), but this does not offer the opportunity of removing impurities as required for the subsequent EW process.⁽¹⁰⁻¹³⁾

[0010] Various strategies have been developed to effect the purification and separation required to obtain high purity products in the form of salts, oxides or metals.

[0011] In the more traditional downstream treatment procedure, the weakly acidic sulphate solution is treated with sulphide to selectively precipitate the base metals and effect removal of other dissolved impurities, mainly Mn, Ca, Mg and other alkaline earth or alkali metals.⁽¹³⁻¹⁵⁾ The main disadvantage of this option is that the precipitate needs to be redissolved by pressure oxidation before further purification and separation of cobalt and nickel can be considered.

[0012] In an alternative option, the base metals are precipitated as hydroxides by neutralising the solution with MgO or CaO.⁽¹⁶⁻²¹⁾ The main advantage of this procedure is that the base metals in the precipitate can be re-leached in ammonia, ammonium sulphate or ammonium carbonate solutions at atmospheric pressure. The main disadvantage, in comparison with sulphide precipitation, is that rejection of manganese and the alkaline earth metals is less efficient as they tend to coprecipitate

with the base metals. They are, however, largely insoluble during leaching but the presence of manganese tends to cause incomplete recovery of nickel and cobalt necessitating an additional strong acid leaching stage to prevent losses of these metals.

5 **[0013]** Further potential solutions are based on SX only, eventually after removal of Fe, Al and Cr by neutralisation/precipitation.

[0014] In one proposed option, base metals are selectively extracted from strongly acidic solutions with a di-thiophosphinic acid commercial extractant (CYANEX 301) leaving Ca, Mg and Mn in the raffinate. Subsequently, the base metals are stripped from the organic phase for further separation and purification. ⁽²²⁾

10 **[0015]** Other systems, under investigation or proposed, usually involve the use of a carboxylic acid (typically Versatic acid), a di-alkyl phosphoric acid (DEHPA) and CYANEX 272 in various configurations. ^(10-12,21) In these instances, Versatic acid is mainly used to remove the majority of Mn, Ca and Mg without major losses of base metals, but does not offer any possibility of separating any of the base metals. It also
15 has the disadvantage of high water solubility at the elevated pH required for effective nickel/cobalt recovery.

[0016] Better rejection of the unwanted impurities, and especially calcium and manganese, can be obtained by adding a synergistic compound to the Versatic acid-containing extraction mixture with an associated reduced pH for effective nickel/cobalt
20 extraction as an added advantage. ⁽²³⁻²⁶⁾ As an alternative, a second extraction can be done on the acidic solution, obtained by stripping the loaded Versatic acid mixture, with a DEHPA based extraction mixture to remove further amounts of calcium and manganese with the added advantage of also removing Zn, Pb, Cd and Cu if present. ^(21,17) However, the use of SX to remove trace amounts of impurities is usually
25 not very cost effective. In addition, extreme care must be taken to avoid losses of nickel/cobalt during this step.

[0017] CYANEX 272 is typically used to separate cobalt and nickel, either before or after partly removing Ca, Mg and Mn impurities using Versatic acid mixtures. However, other base metals, if still present, are co-extracted and special techniques,
30 such as selective stripping, are required to obtain an impurity free solution suitable to produce a high purity product.

[0018] From the preceding comments it is clear that an extraction mixture capable of simplifying the procedure to obtain purified base metal sulphate solutions, suitable to be converted to high purity products, will be of great benefit to the industry as it will reduce the complexity of the processes and the associated costs.

5 OBJECT OF THE INVENTION

[0019] It is an object of the invention to provide a mixture of organic compounds which is suitable to be used as a solvent extractant mixture to treat acidic sulphate solutions and which is capable of:

- a) selectively rejecting unwanted impurities including manganese, lead,
10 alkaline earth metals, alkali metals and ammonium ions;
- b) selectively extracting groups of certain base metals by direct extraction or by differential stripping or by a combination of these; and
- c) selectively removing single base metals by direct extraction or by differential stripping.

15 SUMMARY OF THE INVENTION

[0020] The invention provides an organic solvent extraction mixture which includes:

- (a) a first extractant, which is a substituted imidazole (Diagram 1) or benzimidazole (Diagram 2):

20

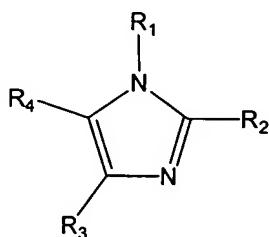


Diagram 1

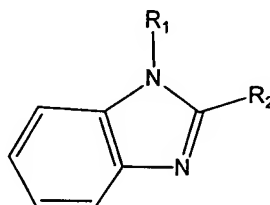


Diagram 2

and wherein the substituents are:

- R₁ = an organic group which:

- is branched or unbranched;
- is saturated or partly unsaturated;
- contains aromatic groups or not;

- is with or without other functional groups; or
- is an esterified fatty acid group;

and wherein R_1 may have between 2 and 20 carbon atoms and preferably has between 6 and 15 carbon atoms;

- 5
- R_3 = a hydrogen atom or a short chain organic group with 1 or 2 carbon atoms, preferably hydrogen or a methyl group;
 - R_4 = a hydrogen atom or a short chain organic group with 1 or 2 carbon atoms, preferably hydrogen or a methyl group;
- 10
- R_2 = a -2-pyridine group in which the pyridine group can be substituted or unsubstituted; or
 - = a -methylene-1-pyrazole group in which the pyrazole group can be substituted or unsubstituted; or
 - = an imidazole based group, which may be a mirror image of the compound shown in Diagram 1 or 2; or
- 15
- = a methylene-amino group as shown in Diagram 3

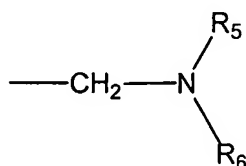


Diagram 3

and wherein

- 20
- R_5 = a hydrogen or a methyl group;
 - R_6 = a hydrogen or an aliphatic group, branched or unbranched, containing between one and 10 carbon atoms; or
 - = a methylene-amino group (see Diagram 3) with one of the substituents being a hydrogen or a methyl group and the other a hydrogen or an aliphatic group, branched or unbranched, containing
- 25
- between one and 10 carbon atoms; or
 - = a -2-pyridine group in which the pyridine group can be substituted or unsubstituted; or

= a -methylene-1-pyrazole group in which the pyrazole group can be substituted or unsubstituted; or

= a 2-methyl imidazole based group which may be a mirror image of the compound shown in Diagram 1 or Diagram 2;

5 b) a non-selective strongly acidic cation second extractant, such as a sulphonic acid ($R-SO_3H$), to facilitate phase transfer of base metal ions from an aqueous weakly acidic sulphate solution into the organic phase, and wherein R is an aliphatic group, either saturated or unsaturated and branched or unbranched, an aromatic organic group or a mixed group consisting of aliphatic and aromatic parts, with
10 between 3 and 40 carbon atoms, preferably with between 8 and 30 carbon atoms;

 c) a modifier to improve the characteristics of the organic phase with respect to metal complex solubility to avoid third phase formation, completeness and ease of stripping, viscosity and phase disengagement; and

 d) a diluent, which is selected from a non-specific aliphatic or aromatic or
15 partly aliphatic, partly aromatic mixture of unspecified composition with a moderate boiling point range and a suitable flash point, such as Kerosene, Shellsol (various grades), Escaid (various grades), Solvesso and similar products.

[0021] The concentration of the first extractant can be between 0.01 and 1.50 Molar, depending on the capacity required and preferably lies between 0.25 and 1.50
20 Molar for commercial applications.

[0022] Typical examples of the second extractant include: di-nonyl naphthalene sulphonic acid (DNNS), di-dodecyl naphthalene sulphonic acid, di-n-octyl methyl sulphonic acid and an alkyl substituted benzene sulphonic acid, all of which are commercially available or easy to synthesise.

25 **[0023]** The concentration of the second extractant may be between 0.001 to 1.0 Molar sulphonic acid, preferably between 0.10 to 0.50 Molar, the optimum being 20% to 25% of the extractant concentration and 50% to 100% of the maximum metal molarity in the organic phase.

[0024] The modifier is preferably characterized by the presence of a sterically
30 available oxygen or nitrogen atom with lone pairs of electrons as in phenols, alcohols,

esters of inorganic and organic acids, ketones, aldehydes, ethers, organic acids, amines and amides.

[0025] The modifier may be added at a concentration of 10% to 70% and preferably at a concentration of 20% to 40% of the total mixture.

5 [0026] The diluent can be added at a concentration sufficient to make up a total of 100% for the mixture,

[0027] Extractions can be carried out in the temperature range between 10°C and 70°C and preferably between ambient and 45°C.

10 [0028] The aqueous pregnant feed solution to be treated can also contain moderate amounts of non-complexing cations, such as nitrate, chlorate or perchlorate, and also appreciable amounts of chloride up to a concentration of 3 Molar.

[0029] Extractions can be carried out at an aqueous pH between 0.0 and 6.0, the preferred pH depending on the objective of the extraction process. This value can readily be estimated from the results given in the Examples by those skilled in the art of
15 solvent extraction-based separations.

[0030] Stripping of the organic phase can readily be effected with a dilute aqueous sulphuric acid solution at a concentration equal to or slightly higher than the change in the metal concentration in the aqueous strip solution during the process of stripping.

20 **BRIEF DESCRIPTION OF THE DRAWINGS**

[0031] The invention is further described by way of examples with reference to the accompanying drawings in which:

[0032] Figures 1, 2 and 3 are flow diagrams of different standard solvent extraction processes, and

25 [0033] Figures 4 to 11 are curves of extraction efficiency as a function of pH for different extractants, with Figures 6 to 11 relating to extractants according to the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0034] The invention can be applied using any standard solvent extraction
30 apparatus, consisting of an extraction section and a single or double stripping section, with an optional washing or scrubbing section in between, and suitable to simulate

standard solvent extraction flow sheets as shown in any of the flow sheets in Figures 1 to 3 respectively.

[0035] The flow sheets shown in Figures 1 to 3 are largely self-explanatory and are known in the art. They are therefore not described in detail hereinafter.

5 **[0036]** In the following examples a comparison is made of the results obtained by using organic solvent extractant mixtures according to the invention and the results obtained using other extractants. Examples 1 and 2 relate to the use of organic extraction mixtures which do not fall inside the scope of the invention while the remaining Examples illustrate results obtained using organic extraction mixtures which
10 fall within the scope of the invention.

Example 1:

[0037] Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.02 Molar DNNS in an iso-decanol (30%) — Shellsol A mixture. The pH of the aqueous phase was adjusted to the target
15 value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction. The results in Figure 4 indicate that DNNS is a
20 non-selective extractant for divalent cations with optimum extraction in the pH range 1.00 to 3.0.

Example 2

[0038] Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.08 Molar 2-(1-butyl-aminomethyl)-
25 1-decylimidazole (BADI) in a mixture containing 30 % iso-decanol and Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The
30 recovered metal in the strip solution was then also determined to calculate and verify the % extraction. The results in Figure 5 indicate that, with BADI only present, only

copper is extracted but from an aqueous bisulphate medium. The other metals are only partly extracted, with an obvious reversal at $\text{pH} \geq 3.50$ when sulphate ions predominate.

Example 3

[0039] Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.08 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) and 0.01 Molar DNNS, in a mixture containing 30 % iso-decanol and Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction.

10 Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

[0040] The results in Figure 6 indicate that, with both BADI and DNNS present, the metals are extracted over a wide pH range giving various opportunities for separations or purifications. One option would be the selective rejection of Zn, Mn, Mg, Ca and Pb from the other compounds presents with a basic flow sheet as shown in Figure 1, with the option of rejecting cobalt or cadmium by appropriate scrubbing (flow sheet as per Figure 2) or selective stripping (flow sheet as per Figure 3). In the absence of iron species, nickel and copper could be extracted selectively at a lower pH,

20 with selective stripping of nickel with a flow sheet as per Figure 3. Obviously, nickel selectivity could also be obtained by prior removal of copper, e.g. by sulphide precipitation.

Example 4

[0041] An aqueous solution of metal sulphates, obtained by bioleaching a nickel sulphide concentrate, after removal of dissolved iron, containing Ni (6.33 g/l), Cu (19.7 ppm), Co (86.3 ppm), Zn (3.3 ppm), Mg (589 ppm) and Mn (11.3 ppm) was contacted with an organic mixture containing 0,57 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) and 0.15 Molar DNNS in a mixture containing 41% iso-decanol in Shellsol A. The pH of the aqueous phase was adjusted to the target value using either

30 aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction.

Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

[0042] The same aqueous solution of metal sulphates was also contacted
5 with an organic mixture containing 1.14 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) and 0.285 Molar DNNS in iso-decanol in the absence of Shellsol A.

[0043] The results in Figure 7a and 7b indicate that, in both instances, nickel
10 can readily be separated from cobalt, zinc, magnesium and manganese using a flow sheet as per Figure 1 or 2. Copper can also be rejected using a flow sheet as per Figure 3.

Example 5

[0044] An aqueous solution of nickel sulphate, at 0.001 Molar, was contacted
15 with an organic mixture containing 0.08 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) and different concentrations of DNNS in a mixture of iso-decanol (30%) and Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to
20 strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

[0045] The results in Figure 8 indicate that complete nickel extraction is
already obtained at a DNNS concentration of 0.005 Molar. Extraction is very effective at DNNS concentrations between 0.010 and 0.040 Molar. With a large excess of DNNS,
25 and up to 0.06 Molar for a 0.001 Molar metal concentration, complete extraction is still possible but only at a higher pH.

Example 6

[0046] Aqueous solutions of nickel sulphate, at 0.001 Molar, were contacted
30 with an organic mixture containing 0.1 Molar 2-(R₅, R₆-aminomethyl)-1-decylimidazole (R-ADI), (R₆ = H, R₅ = methyl, ethyl, butyl, pentyl, hexyl, octyl, ethylhexyl or decyl and R₅ = R₆ = ethyl), 0.010 Molar DNNS in an iso-decanol (30%) – Shellsol A mixture. The

pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

[0047] The results in Figure 9 indicate that very effective metal extraction can be obtained with a mono-substituted amino group, in which the substituent is an aliphatic group containing between one and six carbon atoms. With a longer chain aliphatic substituent or with a double substituted amino group, extraction is less effective, requiring a higher pH for complete extraction.

Example 7

[0048] Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, containing also chloride at a concentration of 0.77 Molar, were contacted with an organic mixture containing 0.08 Molar 2-(1-butyl-aminomethyl)-1-decylimidazole (BADI) and 0.01 Molar DNNS in a mixture of iso-decanol (30%) and Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

[0049] The results in Figure 10, together with those from Example 3 (Figure 6), indicate that the extraction of zinc is strongly enhanced by the presence of chloride in the aqueous phase. The extraction of copper and cobalt is only slightly enhanced and that of nickel is not affected at all. The extractability of manganese remains low and is not much affected either.

[0050] The results show that the presence of chloride, either due to circumstances or by design, is advantageous for the selective separation of certain groups of base metals such as Cu/Zn and rejection of Ca, Mg and Mn from Ni/Co. The

separation between Co and Ni is smaller but remains adequate for effective removal if the cobalt is much lower than that of nickel, which is true in most instances.

Example 8

[0051] Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.08 Molar Bis(2-methyl-1-decylimidazole)amine (BMIA) and 0.01 Molar DNNS, in a mixture containing 70 % isodecanol and Shellsol A. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

[0052] The results in Figure 11 indicate that, with BMIA and DNNS present, the metals are extracted over a wide pH range giving various opportunities for separations or purifications. One option would be the selective rejection of Mn and Mg (and probably Ca and Pb as well) from the other compounds present with a basic flow sheet as shown in Figure 1, with the option of rejecting nickel by appropriate scrubbing (flow sheet as per Figure 2) or selective stripping (flow sheet as per Figure 3). In the absence of iron species, cobalt could be recovered selectively from zinc and copper by selective stripping with a flow sheet as per Figure 3. Overall cobalt selectivity could also be obtained by prior removal of copper and zinc, e.g. by sulphide precipitation.

REFERENCES:

- [0053] 1- J Szymanowski, "Hydroxyoximes and Copper Hydrometallurgy", CRC Press, Boca Raton, USA, 1993.
- [0054] 2- SC Das, PG Krishna, "Effect of Fe(III) during Copper Electrowinning at Higher Current Density", Int. J. Miner. Process., 46, 1996, pp 91.
- [0055] 3- K Tanabe, T Ohgai, T Akiyama and H Fukushima, "Characteristic Behavior of Iron-Group Metals in the Purification Process using Zinc Dust", Proceedings "Zinc & Lead '95", 22-24 May 1995, Sendai, Japan, pp 303.

[0056] 4- K Tozawa, T Nishimura, M Akahori, MA Malaga, "Comparison between Purification Process for Zinc Leach Solutions with Arsenic and Antimony Trioxides", Hydrometallurgy, 30, 1992, pp 445-461.

[0057] 5- ME Chalkley, MJ Collins, IM Masters and E Ozberk, "Department of elements in the Sherritt Zinc Pressure Leach Process", Proceedings "Zinc & Lead '95", 22-24 May 1995, Sendai, Japan, pp 612.

[0058] 6- CJ Krauss, "Effects of Minor Elements on the Production of Electrolytic Zinc from Zinc Sulphide Concentrates", Proceedings International Symposium on Extractive Metallurgy of Zinc, Tokyo, 1985, pp 467-481.

[0059] 7- GL Bolton, VB Sefton, N Zubryckj, " Removal of Manganese and Chloride Ions from Aqueous Acidic Sulphate Solution", US Patent 4,379,037, 1983.

[0060] 8- WR Hopkins, "SX/EW: A Mature but Expanding Technology", Mining Magazine, May 1994, pp 256.

[0061] 9- ML Steemson, GJ Sheehan and DA Winborne, "An Integrated Bioleach/Solvent Extraction Process for Zinc Metal Production from Zinc Concentrates", PCT Patent WO 94/28184, 1994.

[0062] 10-GM Ritcey, NL Hayward and T Salinovich, "The recovery of Nickel and Cobalt from Lateritic Ores" Patent AU 4089096A1, 1996

[0063] 11-AE Norton, JJ Coetzee and SCC Barnett, "An Economically Competitive Process for the Biological Extraction of Nickel", Proceedings "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.

[0064] 12-V Nagel, "Results from the Downstream Unit Operations of an Integrated Pilot-Plant Campaign Using the BioNICTM Process to Produce Nickel Metal Cathode at QNI's Yabulu Refinery", Proceedings "ALTA 2000": Nickel/Cobalt - 6, Perth, Australia, May 15-18, 2000.

[0065] 13-G Motteram, "Black Range Minerals Seyerston Project: A Unique Nickel Laterite", Proceedings "ALTA 2000": Nickel/Cobalt - 6, Perth, Australia, May 15-18, 2000.

[0066] 14-G Motteram, M Ryan, R Berezowsky and R Raudsepp, "Murrin Murrin Nickel/Cobalt Project: Project Development Overview", Proceedings "ALTA 96":

Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 13-14, 1996.

[0067] 15-ME Calkley, R Balan, HU Kranz and R Sanchez, "The Acid Pressure Leach Process for Nickel Cobalt Laterite: A review of Operations at Moa Nickel SA", Proceedings "ALTA 96": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 13-14, 1996.

[0068] 16-A Griffin, "The Marlborough Laterites Project", Proceedings "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.

[0069] 17-P Mason and M Hawker, "Ramu Nickel Process Piloting", Proceedings "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.

[0070] 18-MG Baillie and GC Cock, "Weds Bay Laterite Project, Indonesia", Proceedings "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.

[0071] 19-KJ Hellsten and CR Lewis, "Cawse Nickel Laterite Project", Proceedings "ALTA 96": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 13-14, 1996.

[0072] 20-T Kindred, "Cawse Nickel Operations Process Description and Production Ramp Up", Proceedings "ALTA 2000": Nickel/Cobalt - 6, Perth, Australia, May 15-18, 2000.

[0073] 21-D Jones, J Hestrin and R Moore, "CESL Process for Nickel-Cobalt-Copper Sulphides: Testing in an integrated Pilot Plant", Proceedings "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.

[0074] 22-10 Mihaylov, E Krause, SW Laundry and C van Luong, "Process for the Extraction and Separation of Nickel and/or Cobalt", Canadian Patent CA2145054AA, 1995.

[0075] 23-JS Preston, "Solvent Extraction of Nickel and Cobalt by Mixtures of Carboxylic Acids and Non-chelating Oximes", Hydrometallurgy, 11, 1983, pp 105.

[0076] 24-JS Preston and AC du Preez, "Synergistic Effects in the Solvent Extraction of Some Divalent Metals by Mixtures of Versatic 10 Acid and Pyridinecarboxylate esters", J. Chem. Tech. Biotechnol., 61, 1994, pp 159.

5 **[0077]** 25-JS Preston and AC du Preez, "The Solvent Extraction of Nickel and Cobalt by Mixtures of Carboxylic Acids and Pyridinecarboxylate esters", Solvent Extr. Ion Exch., 13, 1995, pp 465.

[0078] 26-JS Preston and AC du Preez, "Separation of Nickel and Calcium by Solvent Extraction Using Mixtures of Carboxylic Acids and Alkylpyridines", Hydrometallurgy, 58, 2000, pp 239.

10 **[0079]** 27-MJ Dry, G Ioro, DF Jacobs, PM Cole, AM Feather, KC Sole, J Engelbrecht, KC Machett, PJ Cilliers, PT O'Kane and DB Dreisinger, "Cu/Co Tailings Treatment Project, Democratic Republic of Congo", "ALTA 1998": Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum, Perth, Australia, May 25-27, 1998.

15 **[0080]** 28-AM Feather, KC Sole and DB Dreisinger, "Pilot Plant Evaluation of Manganese Removal and Cobalt Purification by Solvent Extraction", Proceedings "ISEC '99": International Solvent Extraction Conference, Barcelona, Spain, 11-16 July 1999.